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Study of Heavy Resins Hydrocarbon Composition for the Pyrolisis of Impulse Nuclea-Magnetic Spectroscopy

Alim Feyzrahmanovich Kemalov*, Ruslan Alimovich Kemalov and Irek Izailovich Mukhamatdinov

Kazan Federal University, Kremlyovskaya St. 18, 420008, Kazan, Russian Federation;
Alim.Feyzrahmanovich2gmail.com, RuslanaKemalov@gmail.com, Mukhamatdinov475@gmail.com

Abstract

One of the areas for an efficient use of large-tonnage and yet scarce binder as bitumen is a broad introduction of bitumen emulsions in water for road and civil construction. The technology of emulsified bitumen preparation, compared with traditional "hot" technologies and the introduction of petroleum solvents has a number of significant advantages. First of all, it is a power-saving technology that does not require heating of the components to high temperatures, which is directly related to the reduction of such combustion products as flue gas and solvent vapor emissions into the atmosphere. Bituminous Emulsion (BE) can be used with some wet mineral material at a reduced temperature that reduces the dependence of work production from weather conditions, thereby prolonging a construction season. The low viscosity of BE allows to distribute the binder material throughout the surface of the mineral materials, which leads to improved accuracy of dosing and the decrease of its flow rate. A high adhesiveness of BE, a layer formation rate and the ability to mechanize many processes as much as possible make Water-Bitumen Emulsions (WBE) the most technologically advanced type of an organic binding material. Petrochemicals are used during the solution of WBE production technology issues satisfying modern requirements. In this aspect, heavy resins of hydrocarbon pyrolisis which are a byproduct and need their rational use are interesting in some extent. The composition and physico-chemical properties of heavy resins of gasoline, ethane and propane-butane fractions pyrolisis produced as the multi tonnage waste at OJSC "Kazanorgsintez" (OTPS) and OJSC "Nizhnekamskneftekhim" (NTPS). Preliminary the samples were obtained at different sampling depth of light fractions by atmospheric distillation original TPS and, respectively, with different initial boiling point. Group hydrocarbon composition of the samples was determined by pulsed NMR[1].

Keywords: Bitumen Emulsions, Complex Structural Units, Heavy Pyrolysis Resins, Hydrocarbon Composition, Modification, Physical - Chemical Properties

1. Introduction

Heavy Pyrolysis Resins (HPR) consists of cyclic, polycyclic, aromatic, acryl substituted aromatic and unsaturated hydrocarbons[1–3]. Such components are capable of strong intermolecular interactions which leads to the formation of Complex Structural Units (CSU) to the structural heterogeneity[3–7]. Such a system is sensitive to external influences. Taking into account these characteristics of HPR composition, the research of the system restructuring, its dynamics at the change of concentration and temperature conditions are of a special interest. To identify these changes, we conducted HPR sample study using the pulsed NMR technique as the most sensitive method to the changes in molecular mobility[7–12].

2. Experimental Part

The composition and physico-chemical properties of heavy resins from gasoline, ethane and propane-butane fractions pyrolisis produced as the multi-tonnage waste at OJSC “Kazanorgsintez” (OTPS) and OJSC “Nizhnekamskneftekhim” (NTPS), the characteristics

* Author for correspondence

and the fractional composition of which are listed in Tables 1 and 2 respectively. The preliminary atmospheric distillation of original TPS allowed to obtain the samples at different sampling depth of light fractions and respectively, at different initial boiling point. The parameters of proton magnetic spin-spin relaxation were determined in the temperature range of 20-100° C which allowed to draw the conclusions about the molecular mobility and structural changes in the samples received HPR samples. The measurements of the spin-spin relaxation periods for T2i were produced using the method of Carr-Purcell-Meiboom-Gill (90°-τ-(180°-2τ) n. During the process of examination the samples were divided into conditional phases "a", "b" and "c" with the spin-spin relaxation periods T2a, T2b and T2c and the population of Pa, Ps and Pc phases, depending on the mobility of hydrogen protons there and the amplitude measurement error did not exceed 2%.

Table 1. Some physical and chemical values of HPR plants at OJSC "Kazanorgsintez" (OJSC "KOS") and OJSC "Nizhnekamskneftekhim" (OJSC "NKNKH")

Indices	HPR OJSC "NKNKH"	HPROJSC "KOS"
Density, kg\m3	1030-1040	1075,0
Coking ability, % wt.	12-16	10,6
Sulfur content, % wt.	0,5	0,2
Relative viscosity at 80 °C, the hole diameter makes 5 mm, s	0,92	1,12
The content of hydrocarbons, % wt.:		
Paraffin-naphthenic	2,1	4,2
Aromatic	57,2	55,8
Content, % wt.		
Resins	20,79	17,7
Asphaltenes	19,91	20,3
Start of boiling, °C	160	94
Flash point (open cup), °C	84	98
Water content, % wt.	0,3-0,5	5-40

Table 2. HPR fractional content

Fractional content (dry matter), % rev.			
HPR OJSC "NKNKH"		HPROJSC "KOS"	
NC-200°C	13	NC-100°C	11
200-220°C	23	100-200°C	9
220-240°C	11	200-300°C	19
240-260°C	13	300-350°C	21
Non-dispersed residue	40	Non-dispersed residue	40

All samples demonstrate polyexponential aspects of enveloping spin-echo signals divided into two or three periods of the spin-spin relaxation. The temperature dependence of the initial HPR OJSC sample "Nizhnekamskneftekhim" indicate the presence of three phases ("a", "b" and "c") in NHPR samples corresponding to the three groups of protons with the relaxation periods T2a, T2b, T2c, which have different molecular mobility (Figure 1), while the sample HPR OJSC "Kazanorgsintez" have only two relaxation periods: T2a and T2b (Figure 2). At that, the values T2c NHPR and T2b OHPR are approximately equal in size, but they have greater exposure to structural changes in NHPR. The obtained data allows to conclude on the presence of highly mobile phase "a" in NHPR, which granted the freedom of NHRP system molecular restructuring. In OHPR the signal of highly mobile light hydrocarbons constituting the dispersion medium is imposed apparently on the signal from water protons, and a small value of relaxation periods T2a and T2b indicates greater OHPR structuring. This behavior of OHPR sample is explained by a high water content - 12%, while in NHRP sample this value is regulated and it makes no more than 0.3-0.5% of wt.

The temperature dependence of relaxation periods in NHPR (Figure 1) show the slope change at 55° C, indicating the decrease in the values of Ea activation energy above this temperature. There are temperature ranges for the phase "c" in which the decrease of T2c periods takes place, which indicates the negative values of Ea, characteristic of spontaneous structural ordering process. For samples TPR is shown in Figure 2, there are no such structural changes for OHRP samples, which may indicate an equilibrium, metastable state of the system.

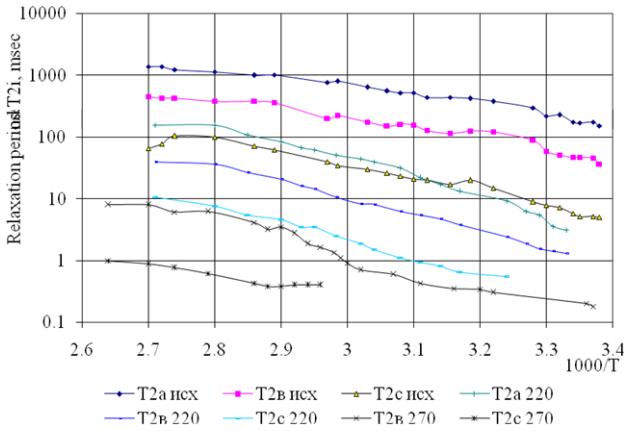

Figure 1. Temperature dependences of HPR relaxation periods at OJSC "Nizhnekamskneftekhim".

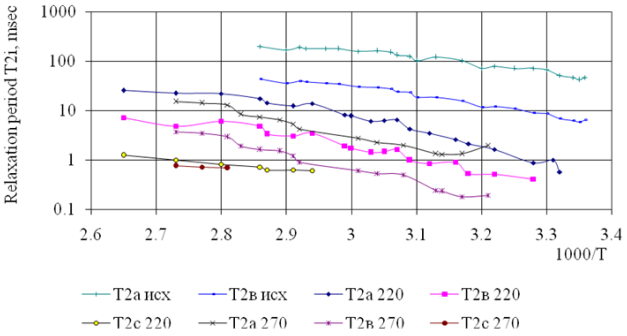

Figure 2. Temperature dependences of HPR relaxation periods at OJSC "Kazanorgsintez".

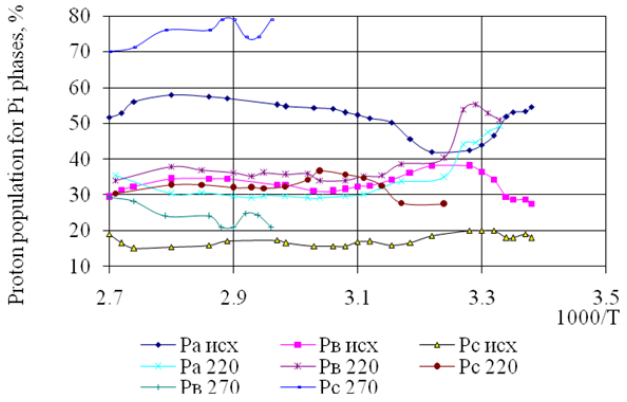

Figure 3. The population dependencies of HRP proton fractions on temperature at OJSC "Nizhnekamskneftekhim".

The temperature dependence of Pc proton populations in NHRP (Figure 3) responsible for the group with the lower mobility of the protons shows the decrease from 20 to 15% with the temperature increase, which can be seen as an increasing relative contribution of less mobile fraction "c" into the fraction "a" by connecting to the molecular movement of the side chains of resins, either due to the reduction of the intermolecular interaction and consequently, the release of the structural frame for a part of highly mobile components. The OHRP demonstrates the reverse pattern of Pc growth from 60 to 75% (Figure 4). This change may be related to the reactions HPR component compaction at the temperature increase. The distillation HRP head fractions results in a sharp decrease of relaxation periods relative to the initial HRP. Thus, the difference of the initial samples is related possibly to the different water content and a significant difference in the number of the least mobile phase "c".

For NHRP and OHRP samples subjected to atmospheric distillation and an initial boiling point of 220° C, the relaxation period values are shown on Figure 2 and Figure 3, respectively, are shorter in order in comparison with the original HRP to all phases. At that the values of T2a, T2b and T2c relaxation periods become close. The actual values of T2c relaxation periods are close to the shortest relaxation periods of oil residues and on this attribute they may belong to the protons on the surface carbon like particles such as asphaltenes, carbenes and carboids.

The values of NHRP proton populations shown in Figure 3 indicate that the selection takes place, as you might expect, due to the fractions "a" and "c", while the value of Pc, at the stripping to 220° C, 4% more than expected concentration change value and this difference increases with the degree of stripping - up to 35% at the stripping to 270° C. The values of the OHRP proton population of a less mobile fraction, significantly exceed the expected values of concentration changes Figure 4.

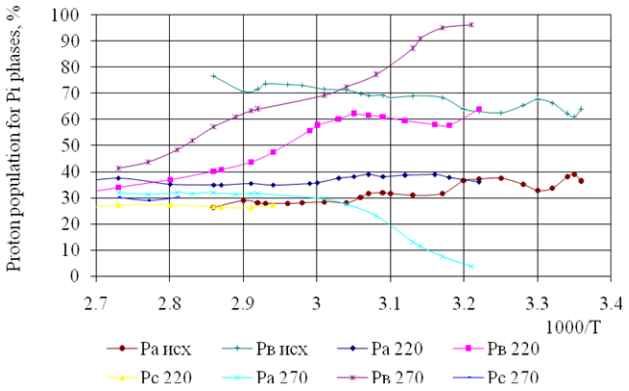

Figure 4. The population dependencies of HRP proton fractions on temperature at OJSC "Kazanorgsintez".

3. Conclusions

As the degree of the stripping phase concentration increases the concentration of phases with the short values of the spin-spin relaxation period is observed. It is significant that this event is related not only to the selection of the light fractions and therefore, to the reduction of the dispersion medium volume, but also, apparently, with the change in the qualitative and quantitative state of Complex Structural Units (CSU) with shorter T2i periods and correspondingly, lower molecular mobility.

The dependences of relaxation periods for the samples with boiling starting point at 270° C indicate a further

decrease of T2a and T2B relaxation periods - by an order for NHRP (Figure 1) and 2-3 times for OHRP (Figure 2). At that T2c values were unchanged compared with the values of the sample at the beginning of boiling at 220° C, although they are observed even at higher temperatures. This indicates the completion of the carbonization process for the phase "c" of OHRP. As the distillation of light fractions and thus the degree of HRP heating a steady increase in Pc, the concentration of the phase, consisting mainly of asphaltenes and carbenes is observed from 15% to 75-80% for the phase "c" of NHRP and up to 100% for the phase "c" of OHRP when light fractions are distilled to 60% of rev.

The samples of residual HRP with the beginning of boiling at 220 and 270° C kept at room temperature for 30 days were re-analyzed. NHRP sample at the beginning of boiling at 220° C a slight increase in Pa was observed, from about 35% to 45%, the decrease in the Pb and Pc from 36% to 32% and from 32% to 27%, respectively, indicating the restructuring of the system, i.e. the passing of the light components from the phase "b" and "c" into the phase "a". The relaxation periods T2a and T2B decreased about 1.5 times, T2c was hardly changed. Analyzing this effect, one may conclude that amid the shortening of relaxation times, testifying to the structuring of the system the release of more mobile phases from the structural CCE cell takes place.

NHRP sample with the beginning of boiling at 270° C, kept at a room temperature for 30 days is characterized by almost constant value of Pa, a slight decrease of Pb (2-3%) and the same increase in Pc. The relaxation times of T2a decreased by 1.5-2 times, T2b decreased 1.5-2.5 times and T2c did not change, which indicates the completion of the component composition development for the heaviest fraction. The reduction of Pb and the growth of Pc indicate the continuation of condensation process and the structuring of light fraction components "b" and the transition of products into phase "c". The samples of OHRP with the beginning of boiling at 220 and 270° C were incubated at a room temperature for 30 days. At that the relaxation period T2a of the sample with b.p. 220° C hardly changed, T2b and T2c decreased by 1.5 times. The populations of Pa protons remained virtually unchanged, Pb decreased by 5-8% and Pc increased by the same amount. The increase in the population of Pc protons and the shortening of relaxation period T2c, show a continuing process of structuring the heaviest fraction, even at a room temperature.

OHRP sample with the beginning of boiling at 270° C is characterized by the decrease of T2a T2b 1.2-1.5 times and the permanence of T2c. Pa decreased by 10-20%, Pb and Pc increased by 8-15% and 3-5%, respectively, which also proves the continuation of the compaction process at a room temperature.

The values of T2c relaxation period of T2c for the analyzed samples correspond to the concentration of paramagnetic centers N = 1021 spin/cm^3 and for the phase "b" with the T2b - N = 1026 spin/cm^3, which corresponds to carbenes and asphaltenes, respectively. Thus, the weighting of the HRP fractional composition leads to spontaneous structural changes as the amount of the least mobile phase "c" exceeds the expected value on concentration change with the simultaneous redistribution of phases, both with their involvement in the structure formation and the release from the structuring process, as during the heating to elevated temperatures and at the curing at a room temperature.

4. Summary

The analysis of changes in relaxation periods and proton populations indicates that the increase of light HRP fractions distillation influences the change in the remainder structure. The weighting of HRP results in increased amounts of asphaltenes and accordingly, to the growth of complex and structural units. Thus, the structure of the original HRP and the HRP after the fraction part distillation and thermal treatment differ significantly.

5. Conflict of Interest

The author confirms that the presented data do not contain any conflict of interest.

6. Acknowledgement

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